Heteroepitaxial growth of InN by microwaveexcited metalorganic vapor phase epitaxy

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Heteroepitaxial growth of InN by microwave-excited metalorganic vapor phase epitaxy

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Epitaxial layers of InN films were grown onto (0001) α-Al_2O_3 substrates in the temperature range of 400–600 °C by microwave-excited metalorganic vapor phase epitaxy using $(CH_3)_3In$ and N_2. Specular surface was obtained at a low substrate temperature (< 500 °C) with a relatively high microwave power (> 100 W). From reflection high-energy electron diffraction analysis, the deposited films were found to be crystalline InN with an orientation relation of (0001) InN//(0001) α-Al_2O_3. The stoichiometry of the grown films was found to be similar to that reported for bulk InN from electron spectroscopy for chemical analysis.

Indium nitride, a III/V compound semiconductor with the wurtzite crystal structure,[1] has a direct band gap ($E_g \sim 1.9$ eV),[2] and so it has the potential for visible light optoelectronic devices and low-cost solar cells with high efficiency. Moreover, the $In_xGa_{1-x}N$ ternary system has attracted attention for *p-n* junction electroluminescence devices emitting blue-violet to orange light, since in this system it is possible to vary the energy gap between 3.46 and 1.9 eV.[3] However, InN has received little attention and has not been investigated enough[4] because it has been difficult to produce single crystalline InN. As far as we know, only one calculated band structure for InN has been reported, by Foley and Tansley,[5] but no assignment for the principal optical transition has been published. Since InN has a low dissociation temperature,[6] it requires a low-temperature growth. Various methods, such as reactive evaporation,[7] reactive rf sputtering,[2,8,9] ion plating,[10] and chemical vapor deposition (CVD),[11] have been explored to obtain InN films. Marasina *et al.*[11] have reported the epitaxial growth of InN on α-Al_2O_3 (0001) and single-crystal quartz by using pyrolysis of $InCl_3$ and NH_3. However, they have not reported the details of the crystal structure of the epitaxial layers.

Recently, microwave plasma and electron cyclotron resonance (ECR) plasma have been used for achieving a low-temperature process. Microwave-excited metalorganic vapor phase epitaxy (microwave-excited MOVPE) has the advantages of low plasma damages in the grown films and no contamination from the electrode. In this letter we report the epitaxial growth of InN on α-Al_2O_3 substrates for the first time by microwave-excited MOVPE and crystal structure of the resulting epitaxial layers.

The schematic diagram of the apparatus for the epitaxial growth of InN is shown in Fig. 1. Substrates were put on the SiC-coated graphite susceptor and heated by a gold image furnace. The substrate temperature was measured by a thermocouple inserted into the susceptor. Trimethylindium [TMI:$(CH_3)_3In$] and pure N_2 were used as the source materials. Since indium chemisorbs only atomic and not molecular nitrogen, it is required to decompose N_2 to obtain InN films. Nitrogen gas was fed into the stainless reaction chamber through the quartz discharge tube and excited by 2.45 GHz microwave radiation. Trimethylindium was maintained at 17 °C and carried with pure N_2 gas into the reaction chamber and mixed with the N_2 plasma just above the substrate. α-Al_2O_3 (0001) substrates were employed and etched in a hot H_3PO_4:H_2SO_4 (1:3) solution for 5 min. The reaction chamber was maintained at a pressure of 1.3 Torr by a rotary pump during the growth. The epitaxial growth was carried out in the temperature range of 400–600 °C. Typical conditions for epitaxial growth are summarized in Table I. The growth rate of InN layers was about 100 Å/min under these conditions.

Figure 2 shows surface scanning electron microscope (SEM) images of the InN layers for various substrate temperatures. At a high substrate temperature (~600 °C), uniform InN layers were not grown. Instead, InN fiber structures and indium droplets were observed as shown in the figure. On the other hand, a specular surface was obtained at a low substrate temperature (< 500 °C) with relatively high microwave power (> 100 W). However, with low microwave power (< 70 W) at the same temperature, InN whiskers were observed on the InN layer. The stability of the InN films is attributed to the partial pressure of atomic nitrogen or excited nitrogen species.[7] In the case of the conventional MOVPE using TMI and N_2 or NH_3 without microwave excitation, only indium droplets have been deposited on the substrates. Since N_2 or NH_3 is hardly decomposed at a temperature below 1000 °C, partial pressure of the active nitrogen species is too low to form the InN. In our works on

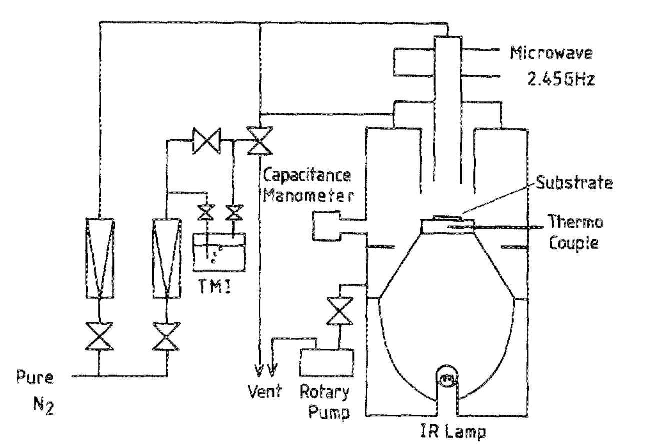

FIG. 1. Schematic diagram of the apparatus for the epitaxial growth of InN.

TABLE I. Growth conditions for the heteroepitaxial layers of InN.

Substrate	α-Al_2O_3(0001)
Substrate temperature (°C)	400–600
TMI flow rate (cc/min, at 17 °C)	50
N_2 flow rate (cc/min)	150
Pressure (Torr)	1.3
Microwave power (W)	50–300

microwave-excited MOVPE, InN films have grown on the substrates, suggesting that the atomic nitrogen or excited nitrogen species are supplied sufficiently by microwave discharge of N_2 gas.

The crystalline structure of the grown films was determined by x-ray diffraction measurements and reflection high-energy electron diffraction (RHEED). From the x-ray diffraction profile, only the (0002) peak was observed and the lattice constant of the c axis determined from the diffraction angle was 5.69 Å, equal to that of InN.[1] RHEED patterns of the InN layers grown at substrate temperatures above 500 °C showed spot patterns. Figures 3(a) and 3(b) show the patterns observed along the $[10\bar{1}0]$ and the $[1\bar{2}10]$ azimuth, respectively. The epitaxial layers have an orientation relationship of (0001)InN//(0001) α-Al_2O_3 substrates. Two arrangements of (0001) InN on (0001) α-Al_2O_3 are possible: $[10\bar{1}0]$InN//$[10\bar{1}0]$ α-Al_2O_3 and $[1\bar{2}10]$InN//$[10\bar{1}0]$$\alpha$-$Al_2O_3$, which have lattice mismatch values of 25.9 and 28.4%, respectively. In Fig. 3(a), weak spots, which agree with the patterns along the $[1\bar{2}10]$ azimuth, can be seen between the main strong spots observed along the $[10\bar{1}0]$ azimuth. This may be attributed to the coexistence of two arrangements in the (0001) plane. This phenomenon may be overcome by choosing the appropriate epitaxial conditions.

The composition of the epitaxial layers was investigated by electron spectroscopy for chemical analysis (ESCA). The peaks for N 1s, In $3d_{3/2}$, and In $3d_{5/2}$ were observed with binding energies of 396.0, 451.0, and 443.4 eV, respectively. The ratio of the peak heights between the N 1s and In 3d peaks of the epitaxial layers was similar to that report-

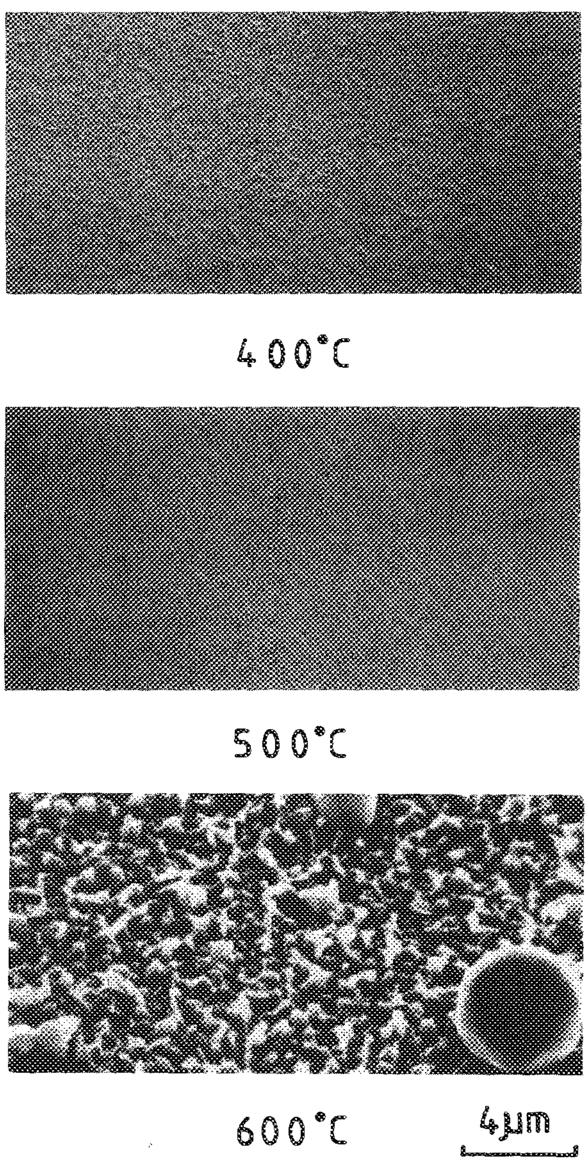

FIG. 2. SEM images of InN on (0001) α-Al_2O_3 substrate in the substrate temperature range of 400–600 °C. Average thickness of the films was ~0.3 μm.

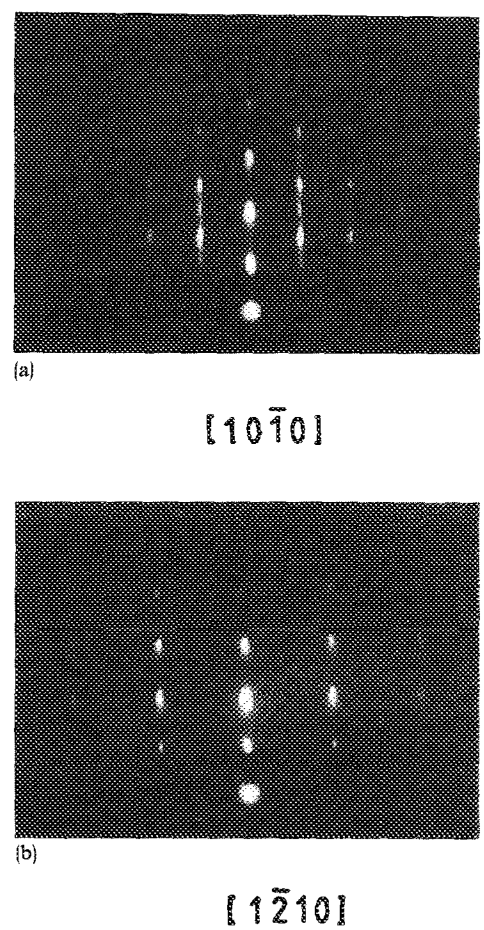

FIG. 3. RHEED patterns of InN films grown on (0001) α-Al_2O_3 at 500 °C. The electron beam is along the (a) $[10\bar{1}0]$ and (b) $[1\bar{2}10]$ azimuth.

ed for bulk InN.[8] This result also suggests that approximately stoichiometric InN epitaxial layers were grown.

In summary, InN epitaxial layers were successfully grown on (0001) α-Al_2O_3 substrates in the temperature range of 400–600 °C by microwave-excited MOVPE using TMI and N_2. The crystalline structure and composition of the grown films were investigated by x-ray diffraction, RHEED, and ESCA analysis. It was shown that (0001) InN layers can be grown on (0001) α-Al_2O_3 substrates at temperatures above 500 °C and that approximately stoichiometric InN layers were grown.

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